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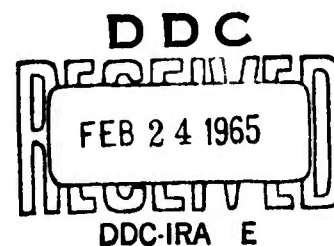
MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

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THIRTEENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 October - 31 December 1964

Contract No. Nonr-3599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P



For

Director
Advanced Research Projects Agency
Washington, D. C.

MRI

MIDWEST RESEARCH INSTITUTE

425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 1-0202

MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

Thomas A. Milne
Frank T. Greene

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PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR.

The report describes additional studies on O and OH radicals in flames, and further attempts to sample condensable species from flames. Modifications and performance of instruments are also discussed.

The research staff consists of Dr. Thomas A. Milne, project leader, Dr. Frank T. Greene and Mr. Jacob Beachey. It is a pleasure to acknowledge the active interest and participation of Mr. Gordon Gross in this research.

Approved for:

MIDWEST RESEARCH INSTITUTE



Sheldon L. Levy, Director
Mathematics and Physics Division

12 February 1965

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SUMMARY

Additional free radical sampling from sheathed H_2-O_2 flames gave O and OH concentration agreeing with previous studies on a simple torch burner. A change in beam modulation frequency from 10 cps to 52 cps gave essentially unchanged sampling behavior. It was determined that beam signals could be measured in the presence of a background of up to 1,000 times the beam intensity. Initial studies on the Fe-O and Fe-O-H systems have failed to yield any gaseous iron-containing species, although orifice plugging rates and sensitivities indicate they should be observed. The species S, SH, and SO have been observed in anomalous ratios when H_2S was added to lean and rich H_2-O_2 flames.

I. INTRODUCTION

Our study of the major effects involved in the quantitative sampling of one atmosphere flames has progressed to the point where the major question remaining is that of the behavior of highly condensable species when sampling with a cooled orifice.

This report describes a few follow-up experiments on free radicals in H_2-O_2 flames, some attempts to detect iron-containing species in flames to which $Fe(CO)_5$ had been added, observation of sulfur species in lean and rich H_2-O_2 flames, and some improvements and tests on the modulated beam detection system.

II. FREE RADICALS AND NONCONDENSABLE SPECIES IN H_2-O_2 FLAMES

In the last report, results of OH and O radical determinations in quite a number of simple torch flames were reported. These studies were all made at only one position in the burnt gas zone and with flames whose temperatures were not measured. As a check on the reasonableness of these results, two flames were chosen for slightly more detailed study. The two flames were burned on a sheathed burner consisting of three 20 gauge stainless steel tubes as the inner burner, surrounded by 24 tubes as the sheath flame. The tubes were all soldered into a water-cooled jacket. With this burner it was possible to make line-reversal temperature measurements in the standard way. The results are shown in Table I.

TABLE I

Flame Composition <u>H_2-O_2</u>	Theoretical Temp. <u>(°K)</u>	Measured Temp. <u>(°K)</u>
2-4	2570	2537 ^(*)
5-1	2627	2612 ^(**)

* The reversal temperature reached a maximum of 2537°K at about 5 mm. from the reaction zone and decreased smoothly at larger distances.

** In this flame the reversal temperature rose over the first 2 cm. to the value indicated and was then constant for several centimeters.

A comparison of the $18^+/17^+$ and $32^+/16^+$ ratios at about 1 mm. beyond the visible reaction zone gave essentially identical results for the sheathed flame and the simple torch flame. Similarly, runs made at chopping frequencies of 10 cps and 52 cps, as described below, gave essentially constant ion ratios.

As part of the proof that a substantial part of the 16^+ and 17^+ ion signals at 20 ev were due to the radicals O and OH, respectively, profiles were measured through the 2-4 sheathed flame of Table I. The results of several runs are given in Fig. 1. The expected excess of O and OH shows up quite distinctly even with the poor spatial resolution afforded by our one atmosphere flames and large sampling orifices. Both radicals appear to peak at the point where the reaction zone just touches the sampling orifice. The 32^+ and 18^+ peaks are not plotted as they remain essentially constant until the sampling orifice penetrates into the unburned gases.

The $18^+/17^+$ ratio at 20 ev was measured in the sheathed 5-1, H_2-O_2 flame 5 cm. downstream and found to be 77, in good agreement with the theoretical H_2O/OH ratio of about 67 and with the value of 52 determined previously in the torch flame. Even if this $18^+/17^+$ ratio of 77 were due solely to the high temperature fragmentation of H_2O , it would still indicate that most of the 17^+ shown for the cooler 2-4 flame in Fig. 1 is due to OH.

There is not yet such a convenient comparison for $32^+/16^+$ as it is much harder to substantially alter the equilibrium, isothermal ratio of O_2/O . The best argument that most of the 16^+ at 20 ev is due to O atoms is the agreement between calculated and observed O_2/O ratios for the variety of flames examined thus far.

A preliminary survey of species in rich and lean H_2-O_2 flames to which H_2S was added indicates that further study of this system will be interesting. In the lean 2-4 H_2-O_2 flame, the observed ratio of SO_2^+/SO^+ was much smaller than JANAF value calculation would indicate for equilibrium. Possible explanations are that the sampling system failed to quench quantitatively, that equilibrium was not reached, that SO_2 fragments very much more extensively at 2500°K than at room temperature or that the free energy used for SO was in error. Each of those reasons would warrant further study of the system.

It was interesting to note that very large total ion signals at 64^+ were observed, which decayed quickly when the mass spectrometer valve to the beam system was closed, but no detectable 64^+ beam contribution was seen, clearly emphasizing the utility of beam modulation. In the rich 5-1 H_2-O_2 flame the species S^+ , SH^+ , and SO^+ were observed. In this case the S^+/SH^+ and S^+/SO^+ were larger than equilibrium calculations would have led us to expect, again indicating the desirability of further studies of this system.

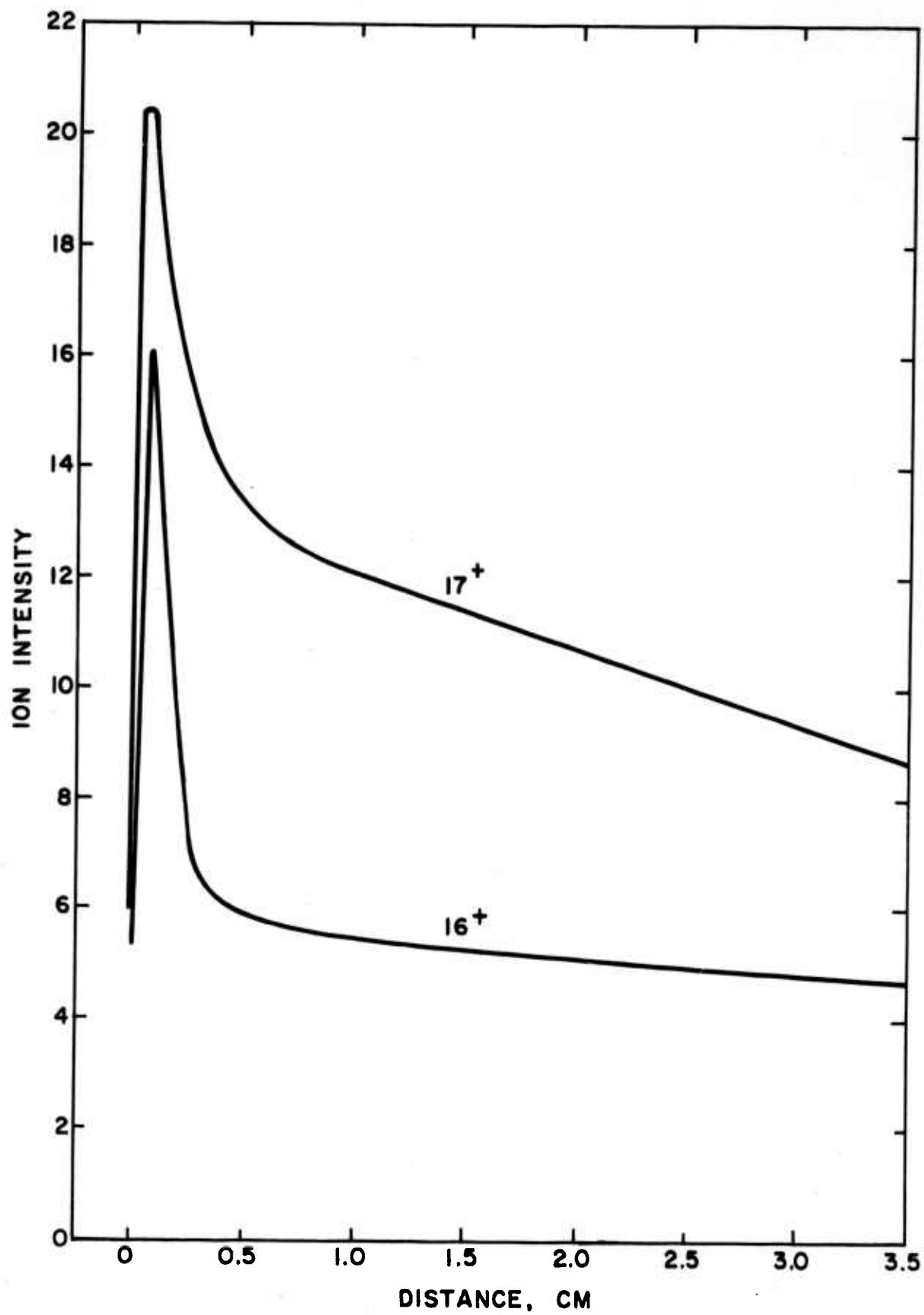


Fig. 1 - Ion Intensity Profiles Through a Lean, 2-4, H_2-O_2 Flame at One Atmosphere. Sampling Orifice is 0.010 in. in Diameter.

III. CONDENSABLE SPECIES

The sampling of gaseous species which yield refractory condensed phases may present several problems not encountered in our previous studies. The relatively cold orifice will eventually be plugged by condensing materials. It is therefore necessary to use quite low concentrations of additives so that data can be obtained before the orifice plugs. It is also possible that heat transfer back through the flame gases may cause shifts in equilibrium or condensation before the species reach the orifice, or that excessive nucleation may take place during the expansion. It is, therefore, important to determine whether condensable species can be observed quantitatively in flames with our present sampling system.

Iron was chosen for the preliminary flame studies of condensable species since it can be readily added as $\text{Fe}(\text{CO})_5$ and since the iron oxides are reasonably refractory. Although the thermodynamics of the iron-oxygen and iron-water systems are not well known, it was hoped that there would be only one or two principal species under any given set of conditions.

Several iron species, including Fe, FeO, and $\text{Fe}(\text{OH})_2$ were sought in stoichiometric CO-O_2 and 2-4 $\text{H}_2\text{-O}_2$ flames. The iron carbonyl was added to the flame in a few per cent argon which had been bubbled through $\text{Fe}(\text{CO})_5$ at 0°C . A maximum of 0.1 per cent total iron was added. Assuming equal transmission and cross sections for Ar and a single iron species, the iron-containing ion should have been detected with a beam-to-background noise ratio of about 4. However, no iron-containing species were observed. This may indicate either that one of the sampling problems outlined above is being encountered or that several iron species are important.

Future work will be directed toward the elucidation of the above question. It will include both a more exhaustive examination of the iron-oxygen species and also the study of thermodynamically better understood systems such as those of silicon-oxygen and titanium-oxygen.

In conjunction with the above experiments the rate of plugging of the orifice was quantitatively determined. The rate of plugging of the orifice was found, as expected, to be nonlinear in time. When 0.1 per cent iron was added to the CO-O_2 flame, the orifice remained substantially open for 4 to 5 min. This is sufficient time to obtain data under normal conditions.

IV. INSTRUMENTAL

Several changes have been made in the modulated beam system being used with the Bendix TOF Mass Spectrometer. The vibrating reed, which functions as the beam chopper, became fatigued and had to be replaced. This opportunity was taken to increase the modulation frequency from a nominal 10 cps to 50 cps. It was hoped that both a better signal-to-noise ratio and better discrimination of beam from scattered beam gases in the ion source might result.

Although these have not yet been carefully checked, no marked improvement has been observed. Some of the data taken at 10 cps have been repeated, but no change has been observed. About the same time a Princeton Applied Research Corporation "Lock-in" Amplifier was obtained in connection with some other work. The lock-in amplifier was found to give slightly better discrimination between beam and background on strong peaks, and to be considerably less time-consuming to operate.

The analog computer arrangement has been replaced with the lock-in amplifier on one channel of the mass spectrometer, and a second lock-in amplifier is on order for use on the other channel.

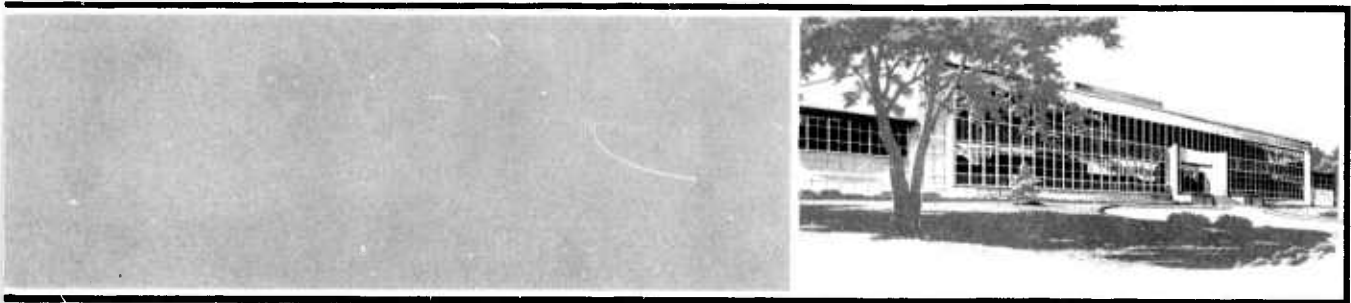
With the system as it now stands, the background to beam discrimination ratio is about 1,000; that is, one should be able to detect a beam signal which is 0.1 per cent of an interfering background peak. This figure was calculated from the peak-to-peak "noise" from various strength background peaks and the known lock-in amplifier sensitivity. It was assumed that a signal could be detected when it was equal to the peak-to-peak noise.

As one check on this discrimination ratio, a weak beam of argon was created by adding about 4 per cent argon to a stoichiometric CO-O_2 flame. The argon beam was then monitored while argon was leaked directly into the ion source. When the total argon signal was about 1,000 times the original beam intensity, it was noted that argon beam intensity had dropped about 30 per cent, presumably due to the rather high argon pressures in the ion source. The above discrimination figure therefore appears to be conservative.

V. FUTURE PLANS

The condensable systems, H-B-O, H-Si-O, H-Ti-O, and H-Fe-O will be studied to try to define the limitations in sampling highly condensable species

and perhaps to add to the thermochemistry of these systems. Further work with the H-S-O system and perhaps with the H-P-O system will also be undertaken. On a related, internally sponsored program, a simple low pressure burner will be set up for sampling studies of the reaction zone of 1/10 to 1/20 atmosphere flames.



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